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# CANADIAN PATENT

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COMPOSITIONS OF POLYMERIC MATERIALS

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No. OF CLAIMS

9 - No drawing

This invention relates to latex-bonded fibre-containing compositions. More particularly, it relates to improved coated papers suitable for printing purposes.

5 The manufacture of coated papers suitable for printing has long been practiced. However changes in the printing industry have resulted in modifications in the property requirements of such paper; typical of such changes is the advent of web off-set printing. Many conflicting properties are sought in coated paper intended for such use, for  
10 example, good adherence of the coating to the fibres (particularly with the increased speed of printing in the web off-set process), good ink receptivity, yet sufficient porosity such as will enable the printed paper to be rapidly dried without blistering.

15 It is an object of this invention to provide a latex composition for preparing an improved paper coating. Another object is to provide a coated paper having in combination good porosity to permit rapid drying without blistering and resistance to "picking" during the printing operation. The term "picking" will be later described herein.  
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It has now been found that improved paper coating compositions may be prepared from a latex composition comprising a mixture of: (A) 10-40 parts on a dry weight basis of an aqueous latex of a copolymer prepared from a monomer  
25 mixture comprising (1) 30-15 weight % of an acyclic conjugated diolefin monomer, (2) 70-85 weight % of a mono-olefinically unsaturated copolymerizable monomer free of carbonyl structures and (3) 0-10 weight % of an olefinically unsaturated carboxylic acid; (B) 90-60 parts on a dry  
30 weight basis of an aqueous latex of a copolymer prepared



from a monomer mixture comprising (1) 0.1-5 weight % of an olefinically-unsaturated carboxylic acid, (2) 0.1-5 weight % of an olefinically unsaturated carbonyl compound, (3) 90-99.8 weight % of monomers composed of 60-30 parts of an acyclic conjugated diolefin monomer and 40-70 parts of a monoolefinically unsaturated copolymerizable monomer free of carbonyl structures.

The invention also provides an improved coated paper whenever prepared from the latex mixture defined herein.

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LATEX A

The conjugated diolefin monomer used to prepare the copolymer of latex A is an acyclic diene having from 4 to 8 carbon atoms as a butadiene-1,3, for example, butadiene-1,3 isoprene, chloroprene and 2,3-dimethylbutadiene-1,3, of which butadiene-1,3 is preferred. The monoolefinically-unsaturated copolymerizable compound free of carbonyl structures may be an alkenyl aromatic compound such as a styrene or a substituted styrene monomer, e.g. alpha-methyl styrene and alpha-chloro-styrene and vinyl toluene with styrene being a particularly useful copolymerizable compound. The benefits to be found within the present concept require that the copolymer of latex A contain 30-15 and preferably 25-20 parts by weight of polymerized diolefin and correspondingly 70-85 and preferably 75-80 parts by weight of the carbonyl-free monomer; that is to say, the copolymer of latex A must be resinous in nature yet comprise sufficient of the diene moiety which normally forms rubbery polymers to provide a balance of properties. In a preferred embodiment, the copolymer of latex A further comprises units of an olefinically unsaturated carboxylic acid comonomer in the amount of up to 10 weight %

of the copolymer, usually from 1-5 weight %. Suitable carboxylic acid monomers include acrylic acid, ethacrylic acid, methacrylic acid, itaconic acid, cinnamic acid and mixtures thereof. When the ethylenically unsaturated carboxylic acid monomer units are present they replace a like amount of the carbonyl structure-free monomer.

#### LATEX B

As to latex B, the conjugated diolefin, the monoolefinically-unsaturated copolymerizable monomer free of carbonyl structures, and the ethylenically-unsaturated acid monomer used to prepare said latex B are each as defined above for latex A.

The olefinically-unsaturated carbonyl compound of the copolymer of latex B is a monomer having an olefinic group and a carbonyl group represented by the general formula:  $H(R_1)C = C(R_2) - C(R_3) = O$  where  $R_1$  is hydrogen or a hydrocarbon radical of 1-6 carbon atoms and  $R_2$  and  $R_3$  are hydrogen atoms or  $C_1 - C_2$  alkyl radicals. Representative examples of carbonyl compounds which can be used in this invention are acrolein,  $\alpha$ -methyl acrolein,  $\beta$ -methyl acrolein,  $\beta$ -phenyl acrolein, methyl vinyl ketone as well as other alkyl vinyl ketones, and their mixtures. Acrolein is the preferred carbonyl compound.

The copolymer of latex B used in accordance with this invention consists of at least four monomer units. The first two monomers, the acyclic conjugated diolefin and the monoolefinically unsaturated carbonyl-free copolymerizable monomer, constitute a major part of the polymer, i.e. 90-99.8 parts per 100 parts by weight of polymer. The proportion of these two monomeric units may vary between 60-30 of diolefin to 40-70 of carbonyl-free monomer but the carbonyl-free

monomer should be present in an amount of at least 40 parts per 100 parts by weight of polymer for use in this invention. The other two monomers of the copolymer of latex B, the carboxylic acid compound and the carbonyl compound, constitute a minor part of the polymer, i.e. a total of 0.2-10 parts per 100 parts by weight of polymer and preferably not more than 6 parts. The amount of carboxylic acid monomer may vary from about 0.1 to 5% by weight of total monomer but preferably is within the range of 1 to 5%, more preferably 1 to 3, particularly when the latex is to be used in paper coatings containing starch. The unsaturated carbonyl compound may be employed in an amount from 0.1 to 5% by weight of total monomer, although 1 to 5 parts are preferred, more preferably 1 to 3. The proportion of the carboxylic acid monomer to the carbonyl monomer may vary within wide limits but it is preferred to maintain it within the range of 3:1 to 1:3 on weight basis.

The polymerization reaction to prepare each of latices A and B is performed in an aqueous emulsion system employing a free radical initiator such as hydrogen peroxide, an alkali metal or ammonium persulphate, azobisisobutyronitrile or a redox initiator pair comprising a reducing compound and an organic peroxide as is well known in the polymerization art. Usually a fraction of a part per 100 parts monomers of a molecular weight regulator such as an alkyl mercaptan containing 8-22 C atoms or a mixture of such mercaptans is employed in the polymerization. The polymerization is carried out in an acidic aqueous medium using one or more synthetic emulsifiers capable of supporting polymerization in an acidic aqueous medium and capable of maintaining a

stable dispersion of the copolymer in both acidic and alkaline mediums; such emulsifiers are known in the art and include various alkyl and alkylaryl sulfonates and polyether sulfates; the amount of emulsifier may vary but is usually about 1 to 3 parts per 100 parts of monomers. Once the acid monomer is incorporated as part of the copolymer, the resulting latex emulsion may be converted to an alkaline pH. The total of the ingredients used in the emulsion polymerization may be added either before the reaction is initiated or part may be incrementally introduced during the reaction. It is preferred to charge initially a portion of the monomer mixture and a portion of the aqueous phase and then add the remainder of these ingredients after the polymerization has been initiated.

The temperature of polymerization may vary as known in the emulsion polymerization art but preferably is between 10° to 80°C. The polymerization is usually conducted to a high degree of conversion of monomers to polymer but it may also be convenient to stop the reaction when 40-65% latex solids are reached and then remove the excess monomer. For most uses, the pH of each latex is adjusted after polymerization from acid, e.g. a pH of 2-6 to alkaline, e.g. a pH of about 7-11.

To prepare the mixture of latices A and B according to this invention, the relative proportion should be chosen so that the mixture contains respectively 10-40 parts of dry weight of latex A and 90-60 parts of dry weight of latex B. Particularly desirable improvements are obtained when the latices are mixed so as to provide weight proportions of 15-25 to 85-75 of the dry weights of latices A and B respectively. In usual practice, the latices will first be

combined and then compounded as for a single latex.

5           The thus prepared latex blend may be combined with  
fibers, e.g. cellulosic fibers, asbestos, fiberglas, by any  
of the conventional methods, shaped if necessary, dried and  
cured. They are particularly useful in preparing compositions  
for the production of coated paper. These compositions are  
aqueous pastes containing between 30 and 70% by weight of  
non-volatile materials such as fillers, adhesives such as  
10           starch and proteins e.g. casein and isolated soy protein,  
polymers, dispersants, buffers and defoamers. The compounding  
techniques, machinery and processes of paper coating are  
described in "Pigmented Coating Processes for Paper and Board"  
TAPPI Monograph Series No. 28 (1964). The filler is selected  
15           from one or more of the conventional fillers such as finely  
divided clays, calcium sulfo-aluminate, calcium carbonate,  
alumina, silica, titania, zinc oxide and colorants and is  
used in amounts from about 1 part to about 20 parts per part  
of uncompounded dry weight solids in the latex and forming  
preferably at least 60% by weight of the total non-volatile  
20           material. A suitable adhesive, e.g. starch is used in an  
amount of 3 to 30 parts dry weight basis per 100 parts filler.  
Proteins such as casein and soy protein can be used instead  
of or in addition to starch. An enzyme-converted starch is  
preferably used.

25           The compositions of this invention show excellent  
binding power and impart improved porosity to the coatings  
thereby providing this much sought-after combination of  
properties. If strength is of less concern or a greater  
strength is obtained than is needed the amount of latex in the  
30           coating composition may be reduced, which feature is valued  
in paper for web off-set printing. The improved porosity

permits faster drying of the coated paper without the occurrence of blistering.

In this specification where the following tests of the coated paper art are referred to, they were performed as follows:

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#### Pick Resistance of Coated Papers

This test is a measure of the adhesion of the coating to paper and indicates the maximum speed at which the paper can be printed without breaking the coated surface.

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A calendered sheet of paper, conditioned for at least 4 hours at 21°C and 50% relative humidity, is printed with an ink of known tack (I.P.I. No. 5) under a known pressure (35 Kg/cm<sup>2</sup>) at different speeds in an I.G.T. (Instituut voor Grafische

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Techniek, Amsterdam, Netherlands) printability tester. The speed at which picking first occurs is the pick resistance value.

#### Ink Absorbency of Coated Papers

This test provides a measure of the quantity of ink that is absorbed by the coated paper. A photoelectric testing meter is used to measure the brightness of the coated paper before and after inking with a standard ink applied in a manner well known in the art. The ink absorbency is expressed as the percentage loss in brightness.

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#### Wet Rub Resistance of Coated Papers

This test measures the amount of the coating that is removed by wet brushing of the coated paper. A model 503 Taber abrader fitted with a rimmed sample holder and with a badger hair brush in place of the grinding wheel is used in this test. A piece of coated paper wetted with 10 mls of water is brushed for a fixed length of time (e.g. 100

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revolutions). The water is collected and then its light transmission is measured and compared to that of the reference water. The wet rub resistance is expressed as the percentage of light transmission.

5 Gurley Porosity

The description of this test is found in the TAPPI Test Method T-460, which was modified as used herein to the extent that a smaller volume (10ccs) of air was used since an alternate method of measuring the time interval to sufficient accuracy was made available.

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Gloss

Determined according to TAPPI Test Method T480TS-65.

Illustration of the invention is provided by the following Examples:

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EXAMPLE I

A number of latex blends were prepared by mixing two latices, A and B, in the dry weight ratios of 10/90, 20/80, 30/70 and 40/60, respectively. The individual latices were identified by the following characteristics:

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Latex A

- |  |               |               |
|--|---------------|---------------|
| - polymeric composition:   | butadiene     | 20.5 weight % |
|  | styrene       | 77            |
|  | itaconic acid | 2.5           |
| - latex solids, weight %   |               | 51            |
| - emulsifier type: anionic, synthetic<br>(sulfonated fatty acid) |               |               |
| - pH   |               | 8.8           |

25

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Latex B

5	- polymeric composition:	butadiene	52 weight %
		styrene	45
		acrylic acid	0.5
		itaconic acid	1.0
		acrolein	1.5
	- latex solids, weight %		49.6
	- emulsifier type:	anionic, synthetic (sulfosuccinate ester)	

10 pH 7.5

With each of the above latex blends a paper coating composition was prepared to a total solids of 60% by weight from the following formulation:

		<u>Parts by Weight</u>
15	Paper coating grade china clay	85
	Precipitated calcium carbonate	15
	Oxidized starch	5
	Latex	12

20 The pH of each coating composition was adjusted to 8.8 and each was found to have satisfactory rheology properties when tested on a Hercules "Hi-Shear" rheometer. With each coating composition a coated paper was prepared by applying the composition to an uncoated paper substrate to a coat weight of 4 pounds per ream by means of a laboratory model coating device. After drying, the coated paper was

25 subjected to testing, the results of which are shown in Table I.

Also prepared and tested was paper coated with a commercial paper-coating latex as a control. This latex had the following properties:

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polymer type - carboxylated butadiene/styrene  
copolymer (60% styrene)

latex solids - 50%

pH - 9.0

5           The results of the experiment show that the coating  
composition of this invention provides a coated paper superior  
to that prepared with the control latex. The improved porosity  
is obtained while retaining an acceptably good level of  
resistance to "picking", while the control although having  
10       a good level of pick resistance had a poor Gurley porosity value.

TABLE I

Ratio	E X P E R I M E N T A L				
	10/90	20/80	30/70	40/60	Control
Pick Resistance - ft./min.	197	196	174	170	193
Ink Absorbency - % loss	19.7	22.1	21.5	20.3	18.4
Wet Rub Resistance - %	97.5	98.0	96.0	96.5	96.0
Gurley Porosity, time (seconds) for 10 ccs. of air to pass	341	302	298	299	465
Gloss - %	61.2	62.9	62.8	64.3	59.0

EXAMPLE II

25           Another latex similar to latex B of Example I was  
prepared but with the butadiene/styrene ratio being 43/54.  
80 parts of this latex (dry weight basis) was blended with 20  
parts (dry weight basis) of latex A of Example I and com-  
pounded in the same way. This coating compound and the  
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Control compound of Example I were applied to a paper substrate at a coating weight of 8 pounds per ream. The two coated papers were dried and tested as in Example I. The results are shown in Table II and clearly point to the superiority of the latex composition of this invention.

TABLE II

<u>Test</u>	<u>Experimental</u>	<u>Control</u>
Pick Resistance - ft./min.	315	255
Ink Absorbency - % loss	18.8	13.9
Wet Rub Resistance - %	93.0	93.0
Gurley Porosity - seconds	580	931
Gloss - %	58.5	57.0

EXAMPLE III

Another latex similar to latex B of Example I was prepared but with the acrolein being omitted from the polymerization recipe. Two paper coating compositions were prepared according to the formulation given in Example I, the one coating utilizing the 20/80 ratio latex blend according to Example I, while the other coating utilizing a latex blend of 20 parts of latex A described in Example I and 80 parts of the present acrolein-free latex. Each of these coating compositions were applied to paper at a coating weight of 10 pounds per ream and the papers were then dried and tested as before. The results as recorded in Table III show clearly the better properties obtained when polymerized acrolein forms part of the molecular structure of the polymer in latex B, particularly in pick resistance and porosity.

TABLE III

Test	Acrolein-Containing Polymer <u>not</u> in Latex		Acrolein-Containing Polymer Present in Latex
Pick Resistance - ft/min	387		426
5 Ink Absorbency - % loss	13.5		18.1
Wet Rub Resistance - %	87.0		98.5
Gurley Porosity - seconds	618		478
Gloss - %	79.9		78.1

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EXAMPLE IV

A coated paper was prepared using a 20/80 latex blend similar to that in Example I except that the latex A in the present example was prepared without the use of an unsaturated carboxylic acid monomer. The coating weight was 10 pounds per ream in the present example. The properties of the coated paper were compared with those obtained using a Control as in Example I also applied at 10 pounds per ream.

TABLE IV

Test	Control		Invention
20 Pick Resistance - ft/min.	335		356
Ink Absorbency - % loss	12.3		16.0
Wet Rub Resistance - %	95.5		95.0
Gurley Porosity - seconds	850		397
Gloss - %	75.1		77.2

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These results demonstrate the improved properties obtained by means of the present invention.

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The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A latex composition comprising a mixture of: (A) 10-40 parts on a dry weight basis of an aqueous latex of a copolymer prepared from a monomer mixture comprising (1) 30-15 weight % of an acyclic  $C_{4-8}$  conjugated diolefin monomer, (2) 70-85 weight % of a monoolefinically unsaturated copolymerizable monomer free of carbonyl structures and (3) 0-10 weight % of an olefinically unsaturated carboxylic acid; (B) 90-60 parts on a dry weight basis of an aqueous latex of a copolymer prepared from a monomer mixture comprising (1) 0.1-5 weight % of an olefinically unsaturated carboxylic acid, (2) 0.1-5 weight % of an olefinically unsaturated carbonyl compound defined by the general formula  $H(R_1)C = C(R_2) - C(R_3) = O$  where  $R_1$  is H or a  $C_{1-6}$  hydrocarbon radical and  $R_2$  and  $R_3$  are H or  $C_{1-2}$  alkyl radicals, (3) 90-99.8 weight % of monomers composed of 60-30 parts of an acyclic  $C_{4-8}$  conjugated diolefin monomer and 40-70 parts of a monoolefinically unsaturated copolymerizable monomer free of carbonyl structures.
2. A latex composition as claimed in Claim 1 wherein the acyclic conjugated diolefin monomer wherever referred to is a butadiene-1,3 and the monoolefinically unsaturated copolymerizable monomer free of carbonyl structures wherever referred to is an alkenyl aromatic compound.
3. A latex composition as claimed in Claim 2 wherein the alkenyl aromatic compound is a styrene.
4. A latex composition as claimed in Claim 3 wherein the olefinically unsaturated carbonyl compound is defined by the general formula  $H(R_1)C = C(R_2) - C(R_3) = O$  where  $R_1$  is a

hydrogen atom or a  $C_{1-6}$  hydrocarbon radical and  $R_2$  and  $R_3$  are hydrogen atoms or  $C_{1-2}$  alkyl radicals.

5. A latex composition as claimed in Claim 4 wherein the olefinically unsaturated carbonyl compound is acrolein and the olefinically unsaturated carboxylic acid wherever referred to is selected from acrylic, methacrylic, itaconic and cinnamic acids and mixtures thereof.

6. A latex composition as claimed in Claim 5 wherein the monomer mixture of (A) comprises (1) 25-20 weight % of said diolefin monomer, (2) 75-80 weight % of said carbonyl structure-free monomer and (3) 1-5 weight % of said carboxylic acid.

7. A latex composition as claimed in Claim 1 wherein the diolefin monomers of (A)(1) and (B)(3) are selected from butadiene-1,3, isoprene, chloroprene and 2,3-dimethylbutadiene-1,3; the carbonyl-free monomers of (A)(2) and (B)(3) are selected from styrene, alpha-methyl styrene, alpha-chloro styrene and vinyl toluene; the carboxylic acids of (A)(3) and (B)(1) are selected from unsaturated  $C_{3-5}$  carboxylic acids and cinnamic acid; and the carbonyl compound of (B)(2) is selected from acrolein, alpha-methyl, beta-methyl and beta-phenyl acroleins and methyl vinyl ketone.

8. A process for producing a coated paper comprising preparing a latex composition according to Claim 1 or 7, adjusting its pH to 7-11, compounding the latex with 1-20 parts by weight of filler per part of latex (dry weight) and 3-30 parts by weight of an adhesive per 100 parts by weight of said filler so that the filler forms at least 60% by weight of the total non-volatile material in the latex composition, spreading the compounded latex composition over a paper sub-

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strate and drying the coated paper.

9. Paper, coated with a composition comprising the latex composition as claimed in Claim 1 or 7.





## IMPROVED COMPOSITIONS OF POLYMERIC MATERIALS

### Abstract of the Disclosure

Improved paper coating compositions may be prepared when the latex used therein comprises a blend of a minor proportion by dry weight basis of a latex of a resinous copolymer with a major proportion by dry weight basis of a latex of a polymer consisting of at least four monomer units, namely, a conjugated diolefin and an alkenyl aromatic constituting 90-99.8% by weight of the copolymer and a carboxylic acid comonomer together with acrolein or methacrolein constituting 0.2 to 10 weight %.